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### COMPLETE SPECIFICATION

#### Improvements relating to the Desulphurisation of Aromatic Hydrocarbons

5 We, THE BRITISH PETROLEUM COMPANY LIMITED, of Britannic House, Finsbury Circus, London, E.C.2., England, a company incorporated in accordance with the Laws of England, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to the desulphurisation of aromatic-containing hydrocarbon fractions by combination of the sulphur with nickel.

15 It is known that in many uses of aromatics, particularly the lower-boiling aromatics such as benzene and toluene, a very low content of sulphur is called for. For example it is desirable that benzene required for hydrogenation to cyclohexane should have a very low sulphur content if the hydrogenation process employed uses a sulphur-sensitive catalyst such as nickel.

20 It is also known that sulphur combines with nickel at moderate temperatures and pressures and hence a process in which the aromatics are desulphurised over nickel is potentially feasible. However, it has been found that for such a process to be effective for long periods it has to be operated in the presence of hydrogen. This is believed to be due to the fact that the sulphur is present as organic sulphur (compounds and that as the sulphur is adsorbed, unsaturated organic radicals are produced which tend to polymerise on the nickel surface and reduce its catalytic activity. If hydrogen is available these unsaturated radicals are hydrogenated to harmless saturated hydrocarbons. The need to have hydrogen present then introduces the risk of hydrogenation of the aromatic hydrocarbons and the practical value of a desulphurisation

process over nickel thus turns on whether it is possible to find conditions in which desulphurisation takes place without appreciable hydrogenation of the aromatic hydrocarbons.

45 The present invention utilises the fact that the hydrogenation activity of nickel declines as the amount of sulphur combined with it increases.

50 According to the present invention therefore a process for the desulphurisation of an aromatic hydrocarbon-containing fraction without appreciable hydrogenation of the aromatic hydrocarbons comprises passing the fraction in the liquid or vapour phase, and in the presence of hydrogen over supported nickel at a temperature and pressure such that sulphur combines with the nickel but below the temperature and pressure at which hydrogen sulphide is produced, said nickel having been pre-sulphided in the absence of hydrogenatable material to a sulphur-nickel atomic ratio such that the nickel has no aromatic hydrogenating activity at the temperature and pressure used for the desulphurisation.

65 The sulphur-nickel atomic ratio at which aromatic hydrogenating activity is lost depends on the temperature and pressure used for the desulphurisation and may be as low as 0.02:1 at low temperatures and pressures (for example 200°F and atmospheric pressure). However since desulphurisation is favoured by higher temperatures and pressures these are preferred and the minimum sulphur nickel atomic ratio is preferably 0.1:1. It has been found that such partially sulphided nickel will continue to absorb sulphur under suitable conditions to a level of at least 0.75:1. Pre-sulphiding to a level above 0.1:1 will not thus render the invention inoperable, but clearly pre-sulphiding to above the minimum level reduces the total desulphurisation cap-

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acidity. The preferred upper limit is thus 0.2:1 and more particularly the preferred limit is 0.12:1.

5 The aromatic hydrocarbon-containing fraction need not consist wholly of aromatics, but if it does not the preferred other components are saturated hydrocarbons. Preferably, however, the feedstock contains at least 95% wt. of aromatic hydrocarbons. The preferred aromatic hydrocarbon is benzene. When the feedstock consists predominantly of aromatic hydrocarbons the sulphur compounds most likely to be present are ring-type sulphur compounds such as thiophenes and substituted thiophenes. The sulphur content will depend on the source and previous history of the feedstock and is not critical. The present invention is, however, particularly suitable for removing relatively small amounts of sulphur, particularly thiophenic sulphur, which are difficult to remove by other processes and for reducing the sulphur content to a very low level. Thus feedstocks with sulphur contents in the range 1 to 50 ppm wt are preferred, sulphur contents of up to 10 ppm wt being especially preferred, and these can be desulphurised to levels of less than 1 ppm wt, more particularly to levels of less than 0.5 ppm wt.

If desired feedstocks containing large amounts of sulphur may be subjected to any of the known catalytic hydrodesulphurisation processes before being desulphurised by the present process. Such known processes should employ catalysts of poor hydrogenation activity, for example cobalt and molybdenum oxides on alumina. Alternatively more than one stage of desulphurisation according to the present process may be used. Both of these alternatives are included within the scope of the present invention. If a preliminary hydrodesulphurisation is carried out hydrogen sulphide produced must be removed before the hydrocarbon material is contacted with the supported nickel.

References to sulphur contents in this specification are to both combined and uncombined sulphur, but are expressed as the element.

The term "without appreciable hydrogenation of the aromatics" means that less than 10 mol % and preferably less than 5 mol % of the aromatics present are hydrogenated.

Since the catalyst used has been presulphided to reduce its aromatic hydrogenating activity the choice of process conditions is wider than if elemental nickel were used.

The process conditions may be selected from the following ranges:

Pressure	0 to 2000 psig (preferably 0 to 1000 psig)
Space Velocity	0.05 to 10 v/v/hr. (preferably 0.2 to 5.0 v/v/hr.)
Inlet hydrogen : hydrocarbon ratio on total feed	0.005 to 10 : 1 molar (preferably 0.02 to 5 : 1 molar)
Temperature	122 to 600° F. (50 to 316° C.) (preferably 167 to 550° F.) (75 to 288° C.)

60 Higher temperatures are preferred, providing that there is no appreciable hydrogenation. Higher pressures favour desulphurisation and can be chosen according to whether operation in liquid or vapour phase conditions is desired. The amount of hydrogen within the above hydrogen to hydrocarbon ratio ranges required to keep the nickel clean may be found by experiment. A substantial excess over this amount would be wasteful and increases the risk of hydrogenation.

75 The supported nickel material used in the present process may be prepared in any of the known ways and may incorporate any of the known natural or synthetic support materials, such as the refractory oxides of the elements of Groups II to V of the Periodic Table, or kieselguhr, pumice or sepiolite. Sepiolite is the

preferred material and the preferred supported nickel material for the process of the invention is nickel on sepiolite prepared and activated according to the disclosures of British Patent No. 899652.

Nickel on sepiolite prepared and activated according to the above-mentioned British Patent may contain from 1 to 50% wt. nickel (expressed as the element) and more particularly from 5 to 25% wt. Such a catalyst has a high nickel surface area and a high sulphur capacity. The sulphur capacity will be proportional to the nickel content, but cost will also increase with increasing nickel content.

The process of the invention may be conducted in liquid or vapour phase or in mixed (gas/liquid) phase. Vapour phase operation is preferred. If in the liquid phase upward flow in the reactor is preferably employed. A fixed

or fluidised catalyst bed may be used. In the latter case high liquid space velocities may cause catalysts to be carried over with the product, in which case a settling tank will be necessary to recover the product.

Clearly the whole of the bed of contact material will have to have the required minimum sulphur:nickel atomic ratio to prevent hydrogenation and in practice it will be the nickel near the reactor outlet which will be sulphided last. This makes uniform sulphiding desirable since otherwise the front end of the bed will be over-sulphided with consequent loss of desulphurisation capacity. By presulphiding according to the present invention in the absence of hydrogenatable material conditions can be chosen which favour uniform sulphiding. The main factors which govern the extent and uniformity of sulphiding are

- (i) the choice of sulphur compound.
- (ii) the temperature at which the sulphur compound is passed over the nickel.
- (iii) the amount of sulphur compound used.
- (iv) the space velocity at which the sulphur compound is passed over the nickel.

The choice of sulphur compound is particularly important since the Applicants have previously found that, when investigating the behaviour of sulphur compounds to nickel, sulphur compounds can be divided into two classes. One class, (referred to as Class A), at temperatures below 392°F, sulphides nickel to a limited extent only which is not exceeded even if excess sulphur is passed over the nickel; the other class (referred to as Class B) continues to sulphide the nickel so long as its passage over the nickel continues.

For the purpose of the present specification we classify sulphur-containing compounds as follows:—

*Class A* Thiophenes, thiocycloalkanes having at least 4 carbon atoms in the ring; and dialkyl-monosulphides.

*Class B* Sulphur containing organic compounds not included in Class A (for example mercaptans, thiacyclobutane and dialkyl disulphides), and elemental sulphur, hydrogen sulphide and carbon disulphide.

Compounds of class A are thus preferred and by suitable adjustment of the temperature in the range 32 to 392°F any desired sulphur-nickel atomic ratio can be obtained up to about 0.25:1. Thus for the particularly preferred range of 0.1 to 0.12:1 the presulphiding temperature will be in the range 284—347°F.

Preferred class A compounds are thiophenes or thiacycloalkanes having from 4 to 10 carbon atoms per molecule, and particularly preferred

compounds are thiophene itself or thiacyclopentane (tetrahydrothiophene).

With class A compounds oversulphiding cannot occur so that the amounts of sulphur compound passed and the space velocity can be chosen to give the required pre-sulphiding in the minimum time.

Compounds of class B may be used if desired but with such compounds careful control of the amount of sulphur passed is required and hence factors (iii) and (iv) above become important. The total amount used should be slightly more than the stoichiometric quantity and the space velocity should be high to encourage uniform sulphiding. The precise amount and space velocity can be determined by a preliminary experiment.

The pre-sulphiding pressure may be in the range atmospheric to 1500 psig, atmospheric pressure being preferred for convenience.

When the hydrocarbon radical released as the sulphur is adsorbed by the nickel is incapable of independent existence, the presence of hydrogen is necessary to hydrogenate it to a stable hydrocarbon. When it is capable of independent existence, the presence of hydrogen is not essential but is still preferred. Thus while the sulphur compounds may sometimes be used by themselves or in a stream of inert gas, it is desirable that they should be used in combination with a stream of hydrogen. Hydrocarbon fractions containing sulphur compounds may also be used, provided the hydrocarbons are not hydrogenatable. Vapour phase conditions are preferred for the pre-sulphiding.

The desulphurisation process of the present invention may be used in any circumstances where desulphurisation of aromatic containing hydrocarbon fractions is required but it is particularly suitable as the first stage of a process for hydrogenating benzene to cyclohexane (i.e. as a guard chamber for benzene hydrogenation). Thus it is particularly suitable for use in combination with the process described in co-pending British Patent Application No. 28767/65 (Serial No. 1144495). It may also be used in combination with the hydrogenation technique described in co-pending British Patent Application No. 41940/65 (Serial No. 1141809).

The invention is illustrated by the following examples:

#### EXAMPLE 1

(a) *Preparation of a partially-sulphided nickel contact material*

0.5 g thiophene were dissolved in 100 ml of n-heptane and the solution passed together with hydrogen over an elemental nickel on sepiolite catalyst (10% wt. nickel) under the following conditions:

Pressure	atmospheric
Temperature	320° F. (160° C.)
Heptane flow rate	2 v/v/hr.
Hydrogen flow rate	300 v/v/hr.

5 The treatment was continued until no further butane and butenes were found in the exit gases. On analysis, the catalyst was found to contain sulphur in a concentration equivalent to a sulphur: nickel atomic ratio of 0.1:1.

(b) *Use of a partially sulphided nickel contact material*

10 A catalyst of 10% wt. elemental nickel on sepiolite which had been sulphided by contact

with thiophene to a sulphur-nickel atomic ratio of 0.1:1, was used to desulphurise benzene containing 22 ppm wt. of sulphur, as thiophenic sulphur. The benzene was passed over the partially sulphided nickel at a space velocity of 1 v/v/hr together with hydrogen at a hydrogen:hydrocarbon ratio of 0.1:1 molar. The temperatures and pressures used and the results obtained are shown in Table 1 below:

TABLE 1

Processing Conditions		S/Ni atomic ratio on catalyst	Product	
Temperature °F.	Pressure psig		Sulphur content ppm wt.	% desulphurization
400	80	0.17 : 1	3.5	84%
400	320	0.25 : 1	2.5	89
500	320	0.31 : 1	1.0	96
"	"	0.40 : 1	1.2	95
"	"	0.50 : 1	2.7	88
"	"	0.60 : 1	3.9	82
"	"	0.70 : 1	4.2	81
"	"	0.748 : 1	6.7	70

25 The table shows the high sulphur capacity of the partially sulphided nickel and the considerable extent of desulphurisation obtained over a period of 1,300 hours. The partially sulphided nickel showed substantially no hydrogenation activity at the temperatures and pressures used.

EXAMPLE 2

A nickel on sepiolite catalyst sulphided as in

Example 1 was used to desulphurise benzene containing 1.6 ppm wt. sulphur. The benzene was passed over the partially sulphided catalyst at a space velocity of 5 v/v/hr. The hydrogen:hydrocarbon ratio was 1.4:1 molar. The other operating conditions and the level of desulphurisation obtained were as follows: —

TABLE 2

Processing Conditions		Catalyst Sulphur : Nickel ratio atomic	Product Sulphur Content ppm wt.
Temperature °F.	Pressure psig		
400	200	0.10 : 1	0.5

## WHAT WE CLAIM IS:—

1. A process for the desulphurisation of an aromatic hydrocarbon-containing fraction without appreciable hydrogenation of the aromatic hydrocarbons, which comprises passing the fraction in the liquid or vapour phase and in the presence of hydrogen over supported nickel at a temperature and pressure such that sulphur combines with the nickel but below the temperature and pressure at which free hydrogen sulphide is produced, said nickel having been pre-sulphided in the absence of hydrogenatable material to a sulphur-nickel atomic ratio such that the nickel has no aromatic hydrogenating activity at the temperature and pressure used for the desulphurisation.
2. A process as claimed in claim 1, in which the said fraction contains at least 95% wt. of aromatic hydrocarbons and from 1 to 50 ppm wt. sulphur.

3. A process as claimed in claim 1 or claim 2, in which the aromatic hydrocarbon is benzene.

4. A process as claimed in any of the preceding claims in which the supported nickel material is nickel on sepiolite containing from 1 to 50% nickel, expressed as the element.

5. A process as claimed in any of the preceding claims in which the said nickel has been presulphided to a sulphur-nickel atomic ratio of from 0.1:1 to 0.2:1.

6. A process as claimed in claim 5 in which the said nickel has been presulphided to a sulphur:nickel atomic ratio of from 0.1:1 to 0.12:1.

7. A process as claimed in any of the preceding claims in which the reaction conditions are chosen from the following ranges:

Pressure	0 to 2000 psig
Space Velocity	0.05 to 10 v/v/hr.
Inlet hydrogen : hydrocarbon ratio on total feed	0.005 to 10 : 1 molar
Temperature	122 to 600° F. (50 to 316° C.)

8. A process as claimed in claim 7 in which the reaction conditions are selected from the following ranges.

Pressure	0 to 1000 psig
Space Velocity	0.2 to 5.0 v/v/hr.
Inlet hydrogen : hydrocarbon ratio on total feed	0.02 to 5 : 1 molar
Temperature	167 to 550° F. (75 to 288° C.)

9. A process as claimed in any of the preceding claims in which the said nickel is presulphided with a sulphur-containing compound

of Class A as hereinbefore set out, at a temperature of from 32 to 392°F.

10. A process as claimed in claim 9 in which

the pre-sulphiding is carried out at a temperature of from 284 to 347°F.

11. A process as claimed in either of claims 9 and 10 in which the sulphur-containing compound is either thiophene or tetrahydrothiophene.
- 5 12. A process as claimed in any of the pre-

ceding claims, substantially as herein described and as illustrated by the examples.

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